

HEAVY METAL ADSORPTION ON THE MUSCOVITE-FULVIC ACID INTERFACE

Sang Soo Lee^{1,2}, Kathryn L. Nagy², Changyong Park¹, and Paul Fenter¹
¹Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439; ²Earth and Environmental Sciences, University of Illinois at Chicago, 845 W Taylor Street, Chicago, IL 60607

INTRODUCTION

Understanding sorption and desorption processes is fundamental to predicting the mobility and bioavailability of heavy metals in aquatic environments. In the Earth surface system, clay minerals are abundant and behave as major sorbents because of their large surface area and surface charge. However, most clay surfaces are coated with natural organic matter (NOM), and the sorbed NOM can change the reactivity of these minerals. To investigate the effect of NOM on metal uptake on clay surfaces, we measured in-situ Resonant Anomalous X-ray Reflectivity (RAXR) from the muscovite (001) surface in contact with four heavy metal (Sr^{2+} , Zn^{2+} , Pb^{2+} , and Hg^{2+}) solutions with and without added fulvic acid (FA). The derived electron-density profiles provide direct insight into the characteristics of the sorbed metal and FA distributions at the interface with an atomic-scale resolution.

In the absence of FA, the derived electron-density profiles show that the metal ions adsorb as both inner-sphere (IS) and outer-sphere (OS) complexes on the muscovite surface. The IS and OS fractionation of the metal ions appears to be controlled by the hydration energy of the elements: Metal ions that hold waters of hydration more strongly adsorb more readily as OS than IS complex on this surface (Fig. 1). In the presence of FA, the adsorbed FA forms an organic film about one nm thick (1), and this organic layer substantially changes the amount and distribution of metal ions sorbed at the interface. For example, the amount of Sr^{2+} sorbed in the near-surface position as an IS complex was reduced when the solution contained FA compared to that without FA, presumably due to competition with FA for the surface sites of muscovite (Fig. 2a). On the other hand, Zn^{2+} , an element which adsorbs mostly as an OS complex, was less affected by the formation of the organic layer, indicating less competition with FA at this larger distance from the interface. In the case of Pb^{2+} , which has a hydration strength that is similar to Sr^{2+} but with a higher organophilicity, the amount of the near-surface fraction did not change significantly, whereas additional metal sorption was observed within the FA film. More dramatic change could be observed for Hg^{2+} , which has the highest affinity for organic matter among four studied metals: In the absence of FA at pH 2, the total amount of adsorbed Hg^{2+} was only 40 % of the amount expected for the full charge compensation of the surface due to competition with hydronium at low pH. However, when FA was present in the solution at the same pH, Hg^{2+} was readily incorporated with FA, and adsorbed as Hg-FA complexes, resulting in about 3 times larger amounts of Hg^{2+} uptake to the FA-free muscovite surface (Fig. 2b).

These results show that the adsorption of metal ions on mineral surfaces depends on their molecular-scale interactions with NOM. How metal ions interact with NOM is related mainly to the hydration strength and organophilicity of metal ions (Fig. 3). These interactions occur within one nm-thick organic layer, and X-ray reflectivity techniques can uniquely distinguish the differences *in-situ* at that scale.

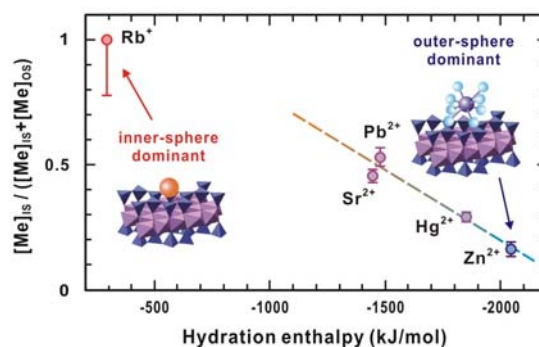


Figure 1. Correlation between the hydration enthalpy and inner- and outer-sphere fractionation of metal ions adsorbed on muscovite (001) surface. [The Rb^+ and Sr^{2+} data are from (2).]

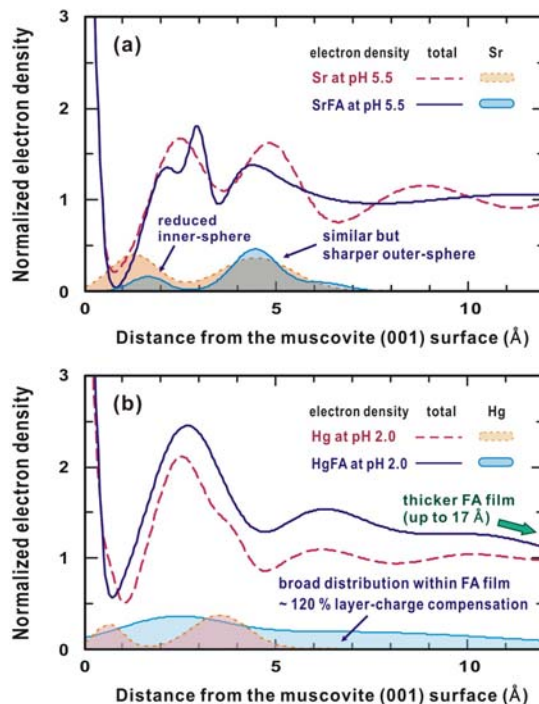


Figure 2. Electron-density profiles at the interfaces of the muscovite (001) surface and solutions containing (a) Sr^{2+} and (b) Hg^{2+} with and without FA. [The electron-density profile of Sr^{2+} at pH 5.5 is from (2).]

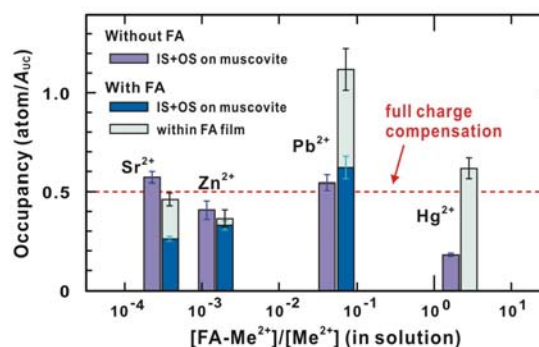


Figure 3. Change of heavy metal uptake to muscovite (001) surface in the presence of dissolved FA as a function of affinity of metal ions for organic matter.

REFERENCES

- (1) S.S. Lee, P.A. Fenter, C. Park and K.L. Nagy. Langmuir, 24, 7817-7829 (2008).
- (2) C. Park, P. A. Fenter, K. L. Nagy and N. C. Sturchio. Phys. Rev. Lett., 97, 016101-4 (2006).